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Structural and luminescence properties of sol-gel derived Cu doped ZnO films

K Das[a], S Ray[a], S Chaudhuri[a] & A B Maity[b]

[a]Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032

[b] School of Applied Sciences, Haldia Institute of Technology, Haldia 721 657

E-mail: abm_hit@yahoo.com

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Well crystallized Cu doped (1, 3 and 5 molar %) ZnO films have been deposited on quartz substrates by sol-gel technique. The microstructural, optical and photoluminescence properties of the films have been studied. It has been observed that the band gap (3.38 eV) of ZnO films did not vary up to 5 molar % of Cu doping. The preferred orientation along (002) was observed for all the films. The X-ray diffraction (XRD) measurement confirmed the decrease of degree of orientation of (002) plane with increasing molar % of Cu in the films. The atomic force microscopy (AFM) measurements have also been performed to examine the surface morphologies of the films. It has been observed that the surface roughness of 1 molar % Cu doped film is smaller (~ 6 nm) than those of 3 and 5 molar % of Cu. The photoluminescence of the films shows prominent peaks between 2.27 to 3.11 eV due to excitonic as well as defect related transitions. A possible mechanism of carrier transitions between shallow and deep impurity levels in the photoluminescence has also been studied.

Keywords: Sol-gel, Cu doping, ZnO film, Microstructure, Photoluminescence

1 Introduction

In recent years, the emphasis on tailor made doped and undoped ZnO materials in bulk and nonostructured forms has attracted much attention of the international research community due to their unique and versatile properties of optical sensing[1], gas sensing[2] and piezoelectric sensing[3] for various applications. A new class of ZnO based microelectromechanical systems (MEMS) like accelerometers, sensors, transducers[3-6] to micro-opto electromechanical systems (MOEMS) and devices such as binary optical lenses, tunable optical filter and optical phase modulator[3,7,8] are under development for specialized applications in the near future. Being wide band gap semiconductor, ZnO is also useful for other possible applications in the field of optoelectronic devices such as ultra-violet (UV) light emitting diodes (LEDs), blue luminescent devices, low threshold room temperature UV lasers, solar cells and photo catalysts[9-12]. Moreover, the interest of this smart material as short wavelength display devices is also receiving greater importance day-by-day over its chief competitor GaN due to its large excitonic binding energy (~ 60 meV), compared to that of GaN (~21-25 meV) and its higher resistance to radiation damage[13] alongwith the possibility of material realization by wet chemical processing technique.

One of the effective approach to tailor the electrical, optical and magnetic properties of this material for various practical applications is the doping with selective elements[14,15]. By choosing suitable rare earth doping, one can modify even the visible emission from ZnO, although there are lots of controversies on the origin of the green emission from it[16-19]. In the present study, the effect of Cu doping (in the range of 1 to 5 molar %) on the morphological changes alongwith the photoluminescence (PL) from ZnO prepared by low-cost sol-gel process has been studied.

2 Experimental Details

The sol was prepared by adding requisite amount of zinc acetate and copper acetate in 2-propanol with continuous stirring at room temperature. The solubility of zinc acetate in 2-propanol being very poor, diethanolamine was added to the sol for total dissolution of the acetate in the mixture. After 12 h of constant stirring, a transparent sol was obtained. By using the dip coating process, the films were deposited on quartz substrates from this sol. The annealing temperature was kept at 800°C in air atmosphere to obtain well-crystallized transparent Cu doped ZnO films. For the desired doping concentration in the films, the molar concentration of copper acetate was varied in the range of 1-5 %.

Figure 1 shows the experimental procedure for preparing the Cu doped zinc oxide films. The crystal structure of the films was determined by using a Seifert-3000P diffractometer with a copper anode and

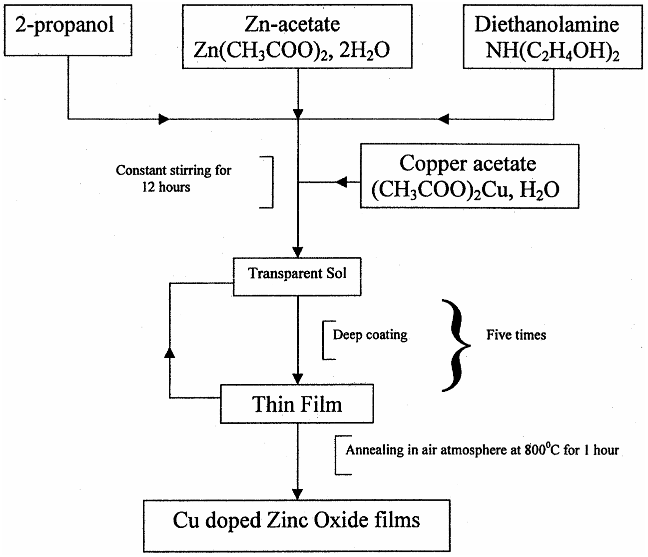

Fig. 1 — Schematic diagram of the detail synthesis procedure of doped ZnO Films

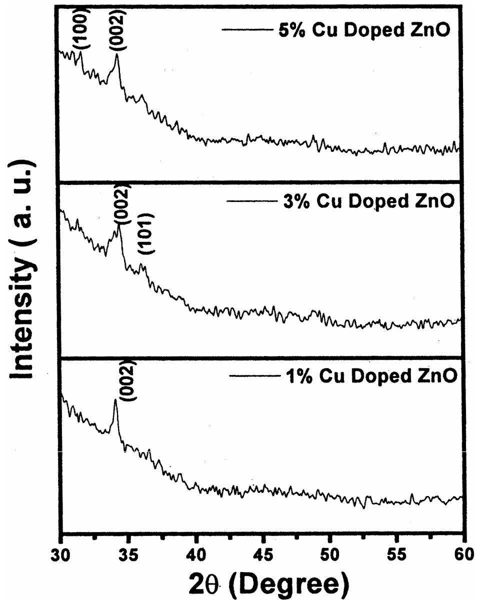

Fig. 2 — XRD pattern of 1 molar % Cu doped ZnO thin film

Table 1 — Degree of orientation along (002) plane of different ZnO films

Cu doping (mol %) copper	Degree of orientation along (002) plane
1	1.00
3	0.65
5	0.57

β-filtering mirror, generating K_α radiation with $\lambda \sim 1.540$ Å, operated at 35 kV and 30 mA. On the other hand, the surface morphologies of the films were investigated by Scanning Electron Microscopy (SEM, Hitachi 52300) and Atomic Force Microscopy (AFM). The optical properties of the films were studied by photoluminescence (PL) measurements, utilizing a Fluorescence Spectrophotometer (F-4500, Hitachi) and transmittance measurements by a spectrophotometer (Hitachi, U-3410). All the structural, morphological and optical measurements were performed at room temperature.

3 Results and Discussion

3.1 Microstructural studies

Figure 2 indicates the XRD patterns of the ZnO films with different molar % Cu. The corresponding analysis confirmed the existence of well crystallized wurtzite structure in all the films. In case of film with 1 molar % Cu, a strong peak (002) of wurtzite ZnO at 34.13° was noticed (Fig. 2). But for other cases, beside this (002) strong peak, additional weak peaks (101) for 3 molar % Cu and (100) for 5 molar % Cu doped films were also observed. The texture of the as-grown ZnO polycrystalline films have been quantitatively examined by estimating the degrees of orientation of a particular peak (002) from the corresponding XRD patterns (Table 1) by using Lotgering formula[20] :

$$F_{\mathrm{hkl}} = \frac{p(hkl) - p_0(hkl)}{1 - p_0(hkl)}$$

where $p(hkl) = I(hkl)/\Sigma I(hkl)$ and $p_0 = I_0(hkl)/\Sigma I_0(hkl)$. Here $I_0(hkl)$ is the (hkl) peak intensity and $\Sigma I_0(hkl)$ is the sum of intensities of all peaks with no prefer orientation, while $I(hkl)$ is the (hkl) peak intensity and $\Sigma I(hkl)$ is the sum of the intensities of all peaks with prefer orientation. Greater resolutions of the peaks were obtained to enable p and p_0 to be determined with reasonable accuracy. From the XRD analysis, a high degree of preferential orientation along (002) plane was evident in the film with 1 molar % of Cu, giving rise to spectra resembling with the single crystal ZnO diffraction pattern. However, the same for other films was found to decrease with increasing molar concentration of Cu in ZnO.

The morphology of Cu doped thin films was observed by SEM and AFM. Figure 3 shows the SEM micrographs, along with the corresponding grain size distribution histogram measured from it for different Cu doped ZnO films. A considerable decrease in average grain size (from 450 to 200 nm) was found with the increase of percentage of Cu molar concentration in ZnO films. From the AFM measurements (Fig. 4), it appeared that the films are

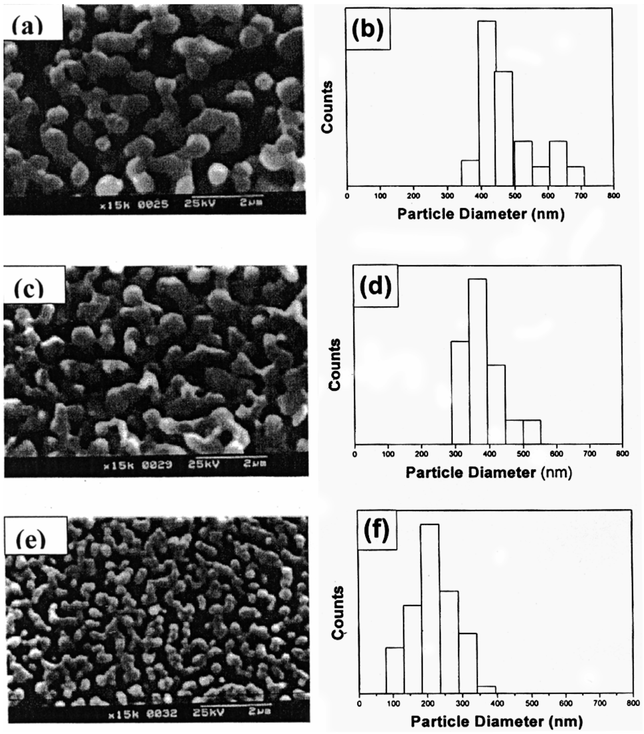

Fig. 3 — SEM image and corresponding particle size histograms of Cu doped ZnO films: (a) & (b) 1 molar %, (c) & (d) 3 molar %, (e) & (f) 5 molar % Cu

mainly close packed crystallites with voids. The amount of voids has found to decrease with the increase of Cu doping. On the other hand, the estimated surface roughness of the films from AFM, has been found to increase from ~ 6 nm for film with 1 molar % Cu to ~ (15-20) nm for films with higher Cu concentration.

3.2 Optical studies

Figure 5 shows the UV-VIS absorption spectra of the films after post deposition annealing at 800 °C in air for 1 h. The absorption spectra revealed a sharp absorption peak at 3.38 eV for all the films. No significant shift of the absorption edge was noted for the increase of doping concentration of Cu upto 5 molar % in ZnO. All the films, before annealing in air, were found to be highly transparent in the visible region.

The most valuable information on the quality and purity of the films may be obtained from the PL measurements. All Cu doped ZnO films showed PL characteristics with the peaks in UV and visible region (Green, Yellow, Orange) between 3.03 to 3.11 eV and 2.27 to 2.75 eV respectively, after laser excitation with wavelength 250 nm (Fig. 6). The UV emission peaks with 3.03 eV (E_2) and 3.11 eV (E_1) as shown in Fig. 6, may be due to the excitonic recombination through single optical phonon or two phonon process[21] near the band edge levels of ZnO. With increasing Cu mole fraction, those excitonic peaks became more prominent. Beside these excitonic

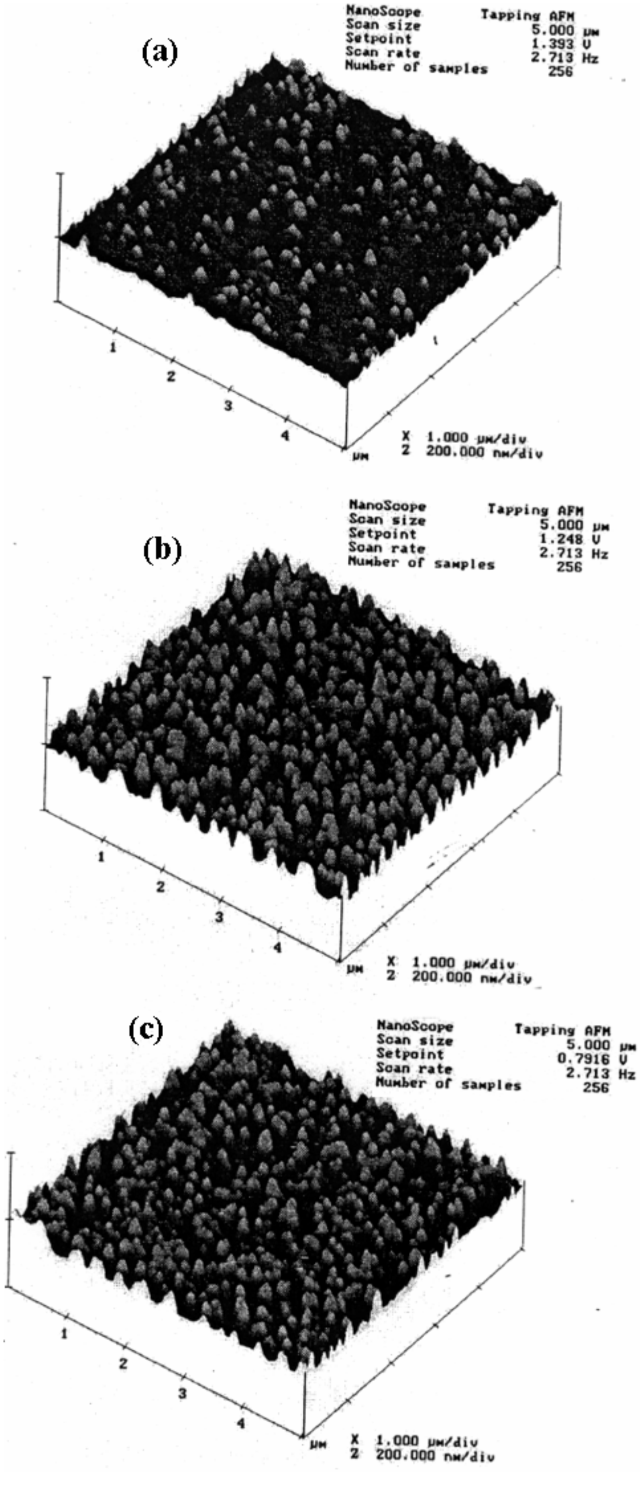

Fig. 4 — AFM images of Cu doped ZnO films: (a) 1 molar %, (b) 3 molar % and (c) 5 molar % Cu

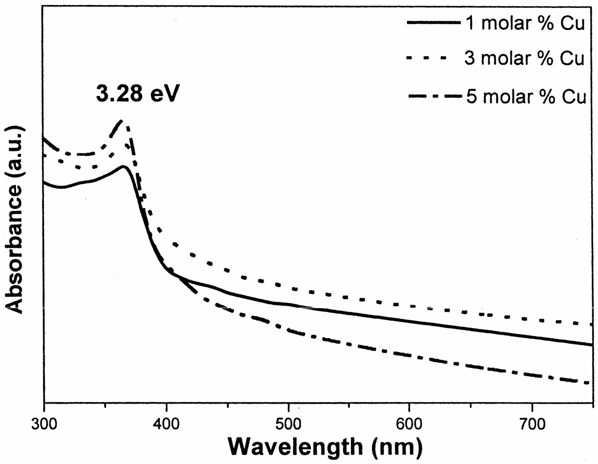

Fig. 5 — Plot of absorbance versus wavelength of 1, 3 and 5 molar % Cu doped ZnO film

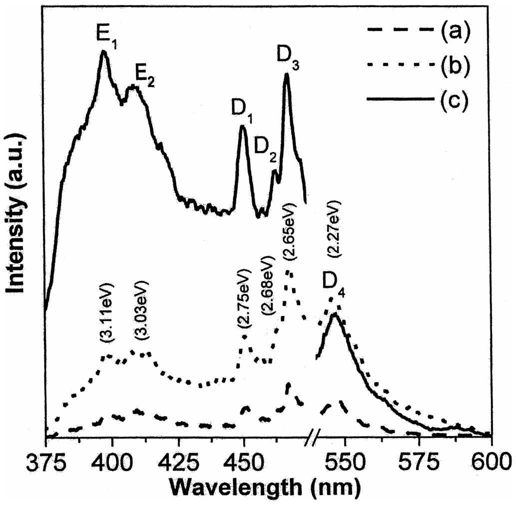

Fig. 6 — Photoluminescence spectra of Cu doped ZnO thin films with excitation wavelength 250 nm : (a) 1 molar %, (b) 3 molar % and (c) 5 molar % Cu

emissions, few more prominent peaks were observed in the visible region of the spectra. The visible emission peaks at 2.75 eV (D_1), 2.68 eV (D_2), 2.65 eV (D_3) and 2.27 eV (D_4) in Cu doped ZnO were for donor-acceptor pair recombination involving different defect levels in the films.

The intensity ratio (Table 2) of the highest excitonic peak (E_1) intensity to that of defect related peaks D_1, D_2 and D_3 has been found to increase with the presence of Cu concentration in ZnO, whereas (I_{E1}/I_{D4}) did not have significant change with Cu concentration up to 3%. However, in the case of 5 molar % Cu doping, the drastic change of (I_{E1}/I_{D4}) enforced the possibility of predominant Cu related defect level induced visible emission from ZnO. It is well known that Cu impurity may provide two defect charge states viz. Cu^+ and Cu^{++} (ref. 14-16). In the films of this study , the Cu^+ defects may be originated by accepting an extra electron from the nearby atom in the lattice of ZnO with configuration $3d^{10}$ $4S^2$. Those defects would act as shallow (singly ionized copper) acceptors widely known as A^- centers, near the valance band of ZnO.

Table 2 — Ratio of the highest excitonic peak intensity (I_{E1}) to that of different defects level in the visible region of PL spectra of Cu doped ZnO films

Cu doping (mol %)	I_{E1}/I_{D1}	I_{E1}/I_{D2}	I_{E1}/I_{D3}	I_{E1}/I_{D4}
1	0.752	0.785	0.413	0.645
3	0.853	0.801	0.504	0.625
5	1.242	1.446	1.061	3.035

With annealing the films in air at 800°C, the Cu^+ ions might be transferred to Cu^{++} or Cu^{2+} with configurations $3d^9 4S^2$ and thereby producing Å centers i.e., neutral copper acceptors[22]. Due to the presence of $4S^2$ electrons, both Cu^+ and Cu^{++} charge states formed covalent bonds with the neighboring oxygen in the lattice. The presence of Cu^{++} ions in the film may be confirmed from the studies of electron paramagnetic resonance (EPR) spectrum[22,24]. Beside the EPR, near infrared (NIR) absorption studies could also confirm the presence of Cu^{2+} ions with its characteristics peaks at 5782 and 5820 cm^{-1} due to internal transitions from $^2T_2$ state to the two $2E$ states[24]. Experimental observation of Garces *et al.*[22] suggested that with the annealing of ZnO, a considerable amount of Cu^{+2} acceptor levels could be added in to the system. Thereby the corresponding Fermi level position should be lowered within the fundamental gap of the material, as the Cu^{+2} level position is shallower than Cu^+ level in it. The average acceptor levels were reported by others[22] to be nearly 50 meV above the valance band of ZnO.

On the other hand, the most probable origin of shallow or deep donor levels may be due to Zn at interstitial position (Zn_i) or oxygen vacancy (O_v) in the material. Recent theoretical calculation[25] confirmed that Zn_i defects would contribute as shallow donors whereas O_v as the deep donor level (~ 60 meV). Based on the correlation between the PL and EPR peak at $g \cong 1.96$, Vanheusden *et al.*[16] suggested that green emission from ZnO was due to carrier transition between singly charged oxygen vacancy (O_v) and photoexcited hole. However, their model raised some controversy. Several workers[22,26, 27] tried to assign EPR $g \cong 1.96$ peak to the shallow donors like Zn_I, not to the O_v^+ level as

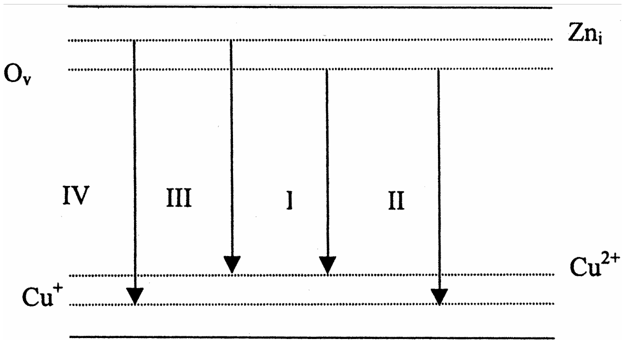

Fig.7 — Schematic diagram of most probable carrier transition in photoluminescence

proposed by Vanheusden *et al*[16]. Moreover, measurements[22,26,27] also confirmed the EPR peak of oxygen valance O_v^+ for parallel and perpendicular magnetic field with the *C* axis at g_{11} = 1.9945 and $g_\perp$ = 1.9960. So, the only alternative explanation of multiple peaks in the visible spectra of PL is due to carrier transitions from shallow and deep donor levels to acceptor levels of Cu^+ and/or Cu^{++} ions in ZnO. The schematic diagram of the most probable carrier transition model for the visible emission in PL is shown in Fig. 7. The different probable transition processes alongwith the corresponding peak values i.e. Transition-I (D_4) at 2.27 eV, Transition-II (D_3) at 2.65 eV, Transition-III (D_2) at 2.68 eV and Transition-IV (D_1) at 2.75 eV are shown in Fig. 7.

Beside those green emissions, several other peaks in the visible spectrum like orange[28] and yellow emission[19,29,30] have also been reported in recent years. The presence of both green and yellow luminescence in ZnO single crystal was confirmed as the emission from Zn_i level by different workers[26,31]. Beside the bulk defect patterns designated above like Zn_I, O_v, O_v^+, Cu^+, Cu^{2+} within the material, one can not also rule out the impact of surface states on the observed PL. It is well known that the material growth process itself inculcated considerable amount of surface defects as well as bulk defects in the material[32].

4 Conclusions

By using the sol-gel technique, preferentially oriented Cu doped ZnO films were successfully synthesized. The microstructural studies confirmed the dense crystal growth with well-defined size distribution of crystal grains in the ZnO films. The atomic force microscopy studies of all the films revealed the relatively smooth surface, with average roughness < 20 nm; while the presence of sharp absorption peak at 3.38 eV from the optical absorption measurement indicates the well crystalline structure of all the films. No as such shift of the band-edge was observed in the films up to 5% Cu doping in ZnO. The photoluminescence spectra of all the films indicated distinct excitonic and defect related peaks with systematic intensity variation with the variation of Cu doping percentage in ZnO. The PL spectra also revealed that the excitonic peak intensity of the films increased by many fold, compared to that of defect related emissions with increasing of Cu concentration in the films. The suggested model of carrier transitions between the shallow and deep impurity levels due to various defect states such as Zn_i, O_v, Cu^+ and Cu^{++} could help to understand the visible emission from Cu doped ZnO films.

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